Structurally characterized bimetallic porphyrin complexes of Pb, Bi, Hg and Tl based on unusual coordination modes

Stéphane Le Gac, Bernard Boitrel

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Stéphane Le Gac and Bernard Boitrel

Institut des Sciences Chimiques de Rennes, UMR CNRS 6226, Université de Rennes1, F-35042 Rennes Cedex, France

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ABSTRACT: This minireview highlights the unusual coordination geometries observed in bimetallic complexes of mercury, thallium, lead and bismuth. These bimetallic complexes remain scarce and through an analysis of their X-ray structures, the various structural features that favorise them will be underlined.

KEYWORDS: X-ray diffraction, bismuth, lead, thallium, mercury, nuclearity.

*Correspondence to: Bernard Boitrel, e-mail: Bernard.Boitrel@univ-rennes1.fr, fax: +33 (0)2-2323-5637; tel: +33 (0)2-2323-5856.

INTRODUCTION

Various metalloporphyrins and isomers are widely found in Nature in order to achieve very precise reactivities. Together with structural variations of the macrocycle such as reduction in chlorin or contraction in corrole, electron or methyl group transfers are efficiently catalyzed [1]. However, one must admit that the regular porphyrin ligand is the base of cofactors in most hemoproteins. Where it is obvious that the ligand itself (free-base porphyrin) is useless for reactivity, all the metalloporphyrins known in Nature are monometallic, that is one metal cation associated with one porphyrin. In some very particular biological cases, one additional binding site above the porphyrin coordination site is supplied to maintain a redox-active metal cation in close proximity of heme [2]. These particularities fully justify why so much work has been devoted to the synthesis, characterization and reactivity of biomimetic heme models [3,4]. Besides its regular tetradentate N4-core binding mode, the porphyrin ligand can also acts as a bi-, tri-, or hexadentate ligand as illustrated by Buchler with his classification of metalloporphyrins in the "Green Book" edited by Kevin Smith [5]. When the macrocycle acts as a hexadentate ligand, it was hypothesized that a bimetallic mononuclear complex was formed between mesoporphyrin IX dimethyl ester and rhenium(I) or technecium(I) salts [6]. The porphyrin acting as a bridging unit was also shown to exist in the case of TPP and mercury as well as TPP and thallium(I) salts by Smith and coworkers [7,8]. These hypotheses have been confirmed later by XRD. As not being related to biological reactivity, these works have been remaining somewhat in the background until more recently, the possibility of preparing such bimetallic complexes was investigated with functionalized porphyrins rather than "naked" ones [9,10]. As this type of complex is of interest in the design of new supramolecular coordination units, in this paper, we will review the bimetallic complexes that have been synthesized from lead, bismuth, mercury, and thallium and for which an X-ray structure has been reported. The "bimetallic" denomination is herein considered as a general interaction between one regular -non-alkylated- porphyrin unit and two metal cations.

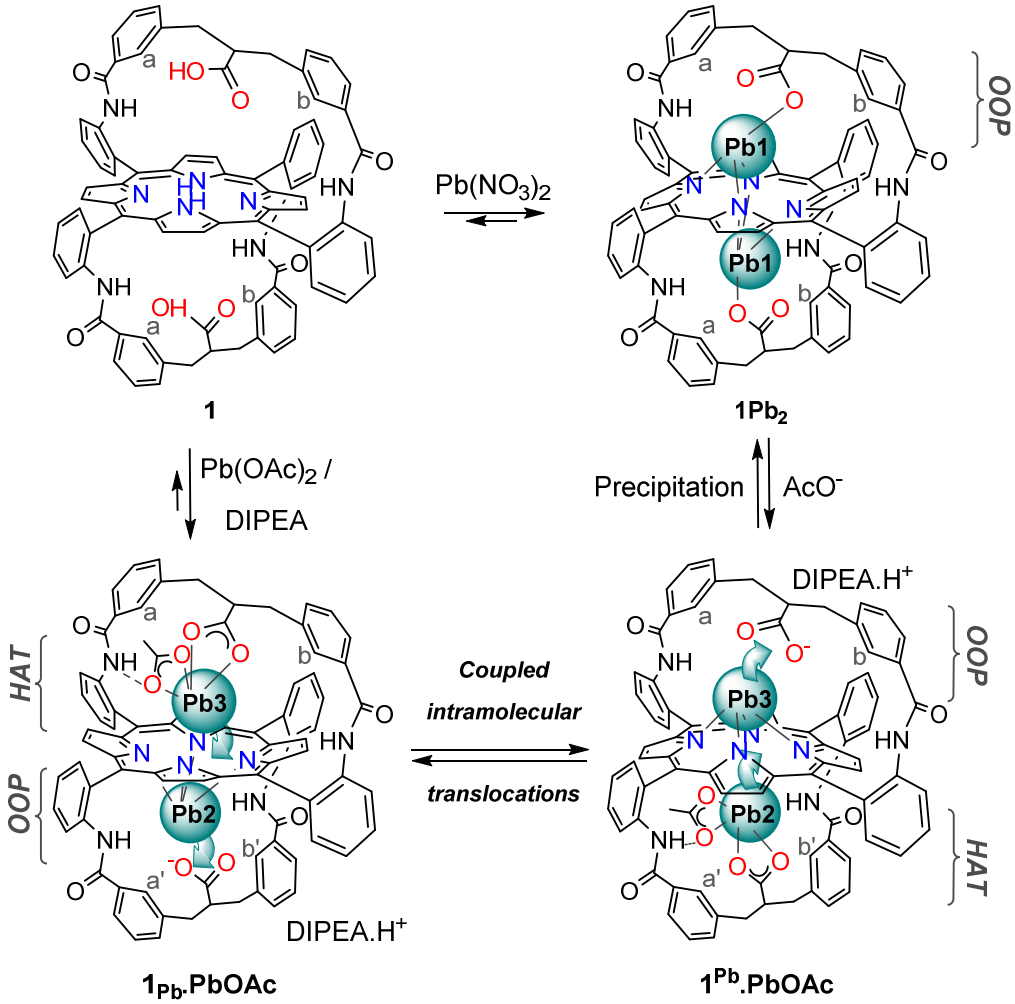
A. LEAD DINUCLEAR PORPHYRIN COMPLEXES

1. Homobimetallic Complexes

Although several types of functionalized porphyrins have been designed to "encage" large cations such as lead, X-ray structures of lead(II) porphyrins remain scarce [11,12,13,14]. The very first X-ray of a homobimetallic lead(II) complex (**1Pb$_2$**) was reported only in 2007 [15]. It was obtained by the room temperature metalation with lead acetate of bis strap porphyrin **1** which delivers an overhanging carboxylic acid on each side of the macrocycle (Scheme 1), followed by precipitation. As we will see later, it has been shown that the same result was achieved by a metallation using an excess of lead nitrate. In proton NMR spectroscopy, this free-base porphyrin **1** being chiral (C_2-symmetry) exhibits 2 singlets of 2 protons each for the aromatic protons of the strap labeled *a* and *b* (see scheme 1, left).

Unexpectedly, the proton NMR spectrum of the resulting lead complex indicates that the two sides of the macrocycle are identical as in the free-base porphyrin **1** with protons Ha and Hb appearing also as two singlets (5.9 and 5.5 ppm). Additionally, the HRMS spectrum of this complex revealed a 2:1 ratio of lead and porphyrin. These results are consistent with the formation of a C_2-symmetric homobimetallic lead complex **1Pb$_2$** and this hypothesis was confirmed by the resolution of its X-ray structure (Figure 1) [15]. This type of complex implies two metal cations, one above and

one below the plane of the porphyrin, bound to 3 adjacent nitrogen atoms from the porphyrin and 3 other bonds with 3 neutral or negatively charged axial ligands. At that time, this peculiar distribution had only been reported for monovalent metals such as Re and Tc as mentionned in the introduction and as Tl as reported by Smith [16] (will be discussed in section D) but was the first instance for a bivalent metal.



Scheme 1. Synthesis of the first homobimetallic lead(II) porphyrin complex **1Pb$_2$** and dynamic behavior of the related complex **1$_{Pb}$.PbOAc**

The macrocyle appears wave-distorted as a consequence of the tilting of two opposite and symmetrically related pyrrole rings (N1-pyrrole and opposite one) towards the lead cation to which it is bound. The angle of the pyrrole plane to the mean porphyrin plane (PyrN1-5MP, 24MP) is 11.03° where 5MP and 24MP stand for pyrrole and porphyrin mean planes composed of 5 and 24 atoms, respectively. Each lead cation remains in an unsymmetrical trigonal antiprism composed of 3 nitrogen atoms from the porphyrin N1, N2, N3, one mono-hapto carboxylate group O4 and two DMSO molecules O5 and O6. N2 and N3 atoms are bound to both lead cations with a distance of 2.787 and 2.648 Å, respectively while the N1-Pb bond as expected, is shorter (2.480 Å). Each lead cation lies 1.795 Å away from the 24MP. The two metal ions, distant of 3.598 Å to each other, are almost positioned over the centre of the porphyrin.

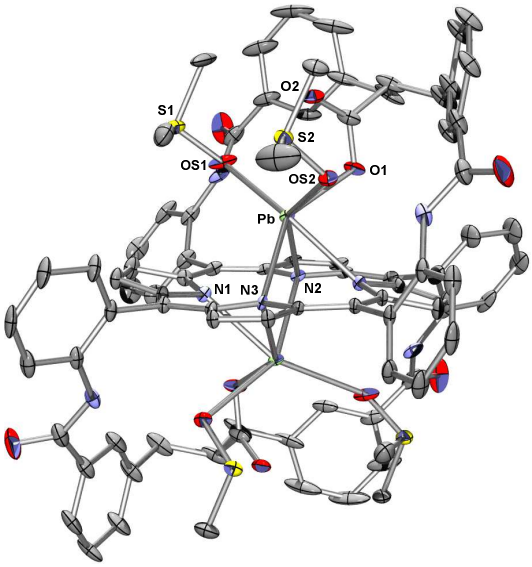
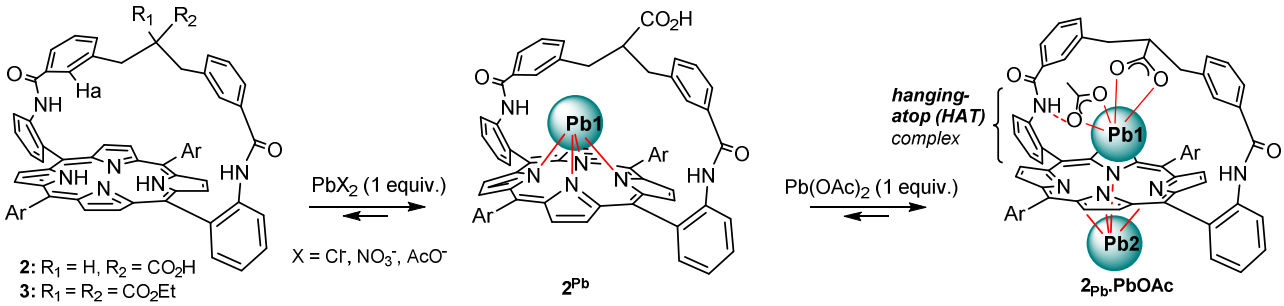


Fig. 1. First X-ray structure of a homobimetallic lead complex **1Pb$_2$**. (distances [Å] and angles [°]: Pb-Pb' 3.598, N1-Pb 2.480, N2-Pb 2.787, N3-Pb 2.648, O1-Pb 2.320, OS2-Pb 2.651, OS1-Pb 2.832, Pb-24-MP 1.795, (PyrN1-5MP, 24MP) 11.03)

Interestingly, DFT calculations were in agreement with a "stereochemically active lone pair of electrons" on each metal cation as some void could be identified in the distribution of bonds and some pockets of residual electron density were found in the vicinity of the lead cations pointing away from the oxygen and nitrogen ligands (hemidirected coordination sphere) [17].

In the previous example, as the intramolecular carboxylate groups are part of the coordination sphere of each lead cation, the dinuclear complex can be rationalized as a result of the symmetry of the ligand. Thus, it was of interest to investigate the metalation of porphyrin **2** (scheme 2), the single strap counterpart of **1**. Indeed, as porphyrin **2** has only one overhanging carboxylic acid group, a symmetrical dinuclear lead complex cannot exist.



Scheme 2. Metalation of single strap porphyrin **2** by various lead salts (Ar = 3,5-dimethoxyphenyl)

The metalation reaction was monitored by proton NMR spectroscopy at room temperature and the addition of 1 equiv. of lead chloride led to the instantaneous and quantitative formation of a new species (C_s symmetry); the addition of an excess of this salt did not induce any further change. This observation is thus in favour of the formation of a monometallic complex. This metal insertion, achieved instantaneously at room temperature, indicates that in comparison with the same metalation with non functionalized porphyrins that requires hard conditions as reflux in pyridine, the binding is assisted by a deconvolution process of the metal carrier by the intramolecular carboxylate group [18]. Therefore, the metal has to be stereoselectively bound inside the cavity as represented for **2^{Pb}** in scheme 2. Furthermore, the fact that the X-ray structure of **3^{Pb}** (**3** being the precursor of **2**, possesses two overhanging carbethoxy

groups) clearly exhibits lead sitting inside the cavity is a supplemental and consistent observation for such a stereoselective deconvolution mechanism [19].

At the opposite of what was described here above, if a second equivalent of $Pb(OAc)_2$ (instead of $PbCl_2$) is added to $\mathbf{2}^{\mathbf{Pb}}$, a second coordination process is observed with the quasi-quantitative formation of a new species. A ROESY 2D NMR experiment of the latter revealed that one acetate counteranion is part of this new complex. The highfield shift for the CH_3 protons of this acetate (c.a. 1.6 ppm relative to the free acetate anions) indicates a bound acetate located above the porphyrin plane. X-ray diffraction analysis confirmed the bimetallic nature of this complex, subsequently named $\mathbf{2_{Pb}.PbOAc}$, and represented in scheme 2. The nomenclature of the complex indicates one Pb cation (in subscripted letters) located on the bottom side of the macrocycle and "PbOAc" (in full letters) indicates the second Pb cation without any direct interaction with the N-core of the porphyrin as detailed hereafter (Figure 2). Indeed, Pb2 is 4-coordinate to the N-core of the porphyrin on the open side opposite to the strapped side and 1.383 Å out of the porphyrin mean plane. The second lead cation (Pb1) has no bond with the porphyrin N-core (average Pb1-N = 3.243 Å), but is hung 2.323 Å above the porphyrin mean plane. Its coordination sphere involves two dihapto carboxylate ligands, one intramolecular from the strap and a second exogenous one, and is completed by one DMSO ligand. All the ligands of this second lead cation are obviously located in one part of the encompassing space; this strongly hemidirected distribution of the ligands was ascribed to the lone pair of lead which points towards the dome-distorted N-core of the macrocycle. Both the exogenous acetate and DMSO ligands are oriented at almost 90° relative to the carboxylate of the strap and are H-bound to one amide NH group (dashed lines in Figure 2). There is no metal-metal interaction (Pb-Pb distance of 3.727 Å that is 92 % of the sum of lead Van der Waals radii). From these structural data, the lead cation inside the cavity appears as "floating" above the porphyrin, in what was defined as the *hanging-atop* (HAT) coordination mode relatively to the *sitting-atop* (SAT) intermediate of Fleischer. As will be detailed later in this minireview, this HAT new coordination mode has been extented to other metal cations and to heterodinuclear complexes. Actually, the three prerequisites to observe this HAT coordination mode are first a structure with a strap bearing an overhanging carboxylate group, second the presence of acetate anions in the medium and, third a dome-distorted porphyrin. Usually, this domed distortion of the macrocycle is achieved by the coordination of a large cation (as Pb(II), Bi(III), Cd(II), Hg(II), Tl(III)) into the macrocycle. This HAT coordination mode is also at the origin of new dynamic processes by which two cations exchange either their locations or their coordination modes or both, but this is beyong the scope of this review.

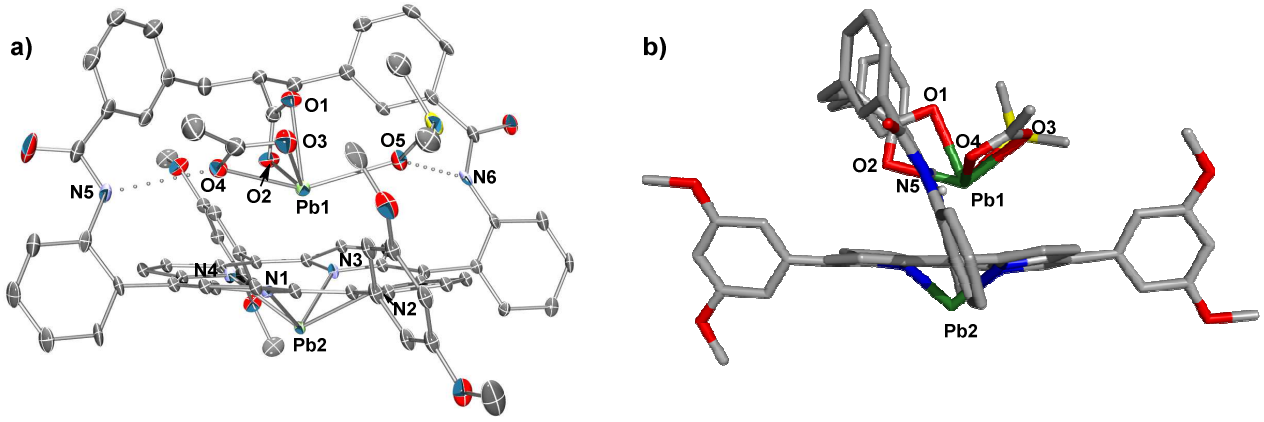


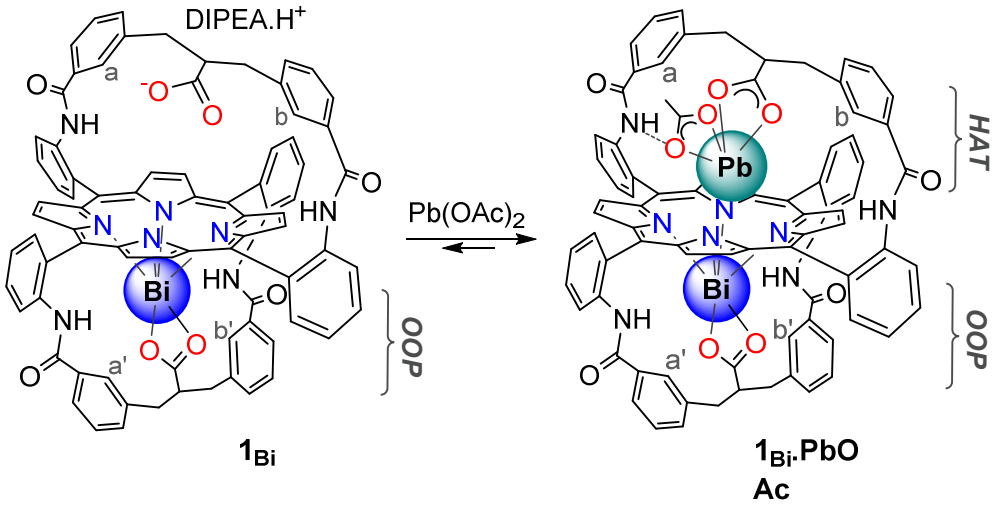
Fig. 2. X-ray structure of homobimetallic lead complex $\mathbf{2_{Pb}.PbOAc}$. (a) perspective ORTEP view, (b) Side view indicating the bending of the strap to accomodate the HAT Pb1. (Distances [Å]: Pb1-Pb2 3.727; Pb2(/Pb1) to 24-atom mean plane 1.383(/2.323);

Pb1-O1 2.449, Pb1-O2 2.380, Pb1-O3 2.587, Pb1-O4 2.432, Pb1-O5 2.596, Pb2-N1 2.399, Pb2-N2 2.413, Pb2-N3 2.405, Pb2-N4 2.381, N5-O4 2.963, N6-O5 3.090)

Consequently, further studies back with the bis strap ligand **1** established that the coordination behavior towards lead acetate in solution was different [20]. The titration experiment in the presence of diisopropylethylamine (DIPEA) evidenced a highly cooperative process as only one complex was observed with a C_2-symmetrical pattern but significantly broadened and with a new signal at 0.3 ppm, reminding us the bound acetate found in **2_{Pb}.PbOAc**. As the signal of the free acetate anions was also large, indicating their implication in an exchange process, it was verified that the dinuclear species displays some fluxionality in the presence of acetate anions. Indeed, low temperature measurements evidenced a single species with a dissymmetric pattern, with four singlets for protons Ha,b,a',b' in the 5-6 ppm region together with a sharp singlet integrating for three protons at 0.24 ppm. This dissymmetric species was attributed to the bis-strap counterpart of **2_{Pb}.PbOAc** and exhibited a fluxionality, **1_{Pb}.PbOAc** ⇆ **1^{Pb}.PbOAc** (Scheme 1, bottom line). Both cations exchange both their locations (N4-core/strap) and their coordination modes (OOP/HAT) while staying on their respective side of the macrocycle. Said another way, each cation is free to cotranslocate with the other one but is restrained on one side of the porphyrin (compartmentalized motion).

2. Heterobimetallic complexes

The bis-strap porphyrin **1** is obviously suitable for the coordination of trivalent cations as thallium(III) or bismuth(III) as these cations are known to form porphyrin complexes with a monohapto or bishapto axial ligand [21,22]. As a matter of fact, its metalation with these two cations has already been reported and was achieved easily at room temperature. The X-ray structures of both bismuth complex **1_{Bi}** [15] and thallium complex **1_{Tl}** [23] have also been resolved and exhibit monometallic complexes in which the intramolecular carboxylate group is bound as a bishapto ligand to the out-of-plane (OOP) metal with distances to the 24MP of 1.309 Å in **1_{Bi}** and 0.914 Å in **1_{Tl}**.



Scheme 3. Metalation of bis strap metalloporphyrin **1_{Bi}** by lead acetate

Thus, the binding properties of **1_{Bi}** towards Pb(II) were investigated by ^{1}H NMR spectroscopy in DMSO-d_6 solution, without DIPEA [20]. This complex was fully consumed upon addition of one equiv. of $Pb(OAc)_2$. The corresponding NMR spectrum was characterized by 4 broad singlets for Ha,b,a',b' protons (see Scheme 3), in agreement with the

formation of a dissymmetric species. A broad signal of 3 protons was also observed at 0.36 ppm, consistent with a single acetate molecule included in this complex. This chemical shift of 0.36 ppm for the bound acetate compares well with that of a PbOAc moiety (*ca.* 0.30 ppm for **2_{Pb}.PbOAc**), and therefore from these NMR data, the formation of the heterobimetallic complex **1_{Bi}.PbOAc** (Scheme 3), with Bi(III) and Pb(II) respectively in OOP and HAT coordination modes is expected. This hypothesis was verified by an X-ray structure obtained from single crystals grown upon slow evaporation of the NMR tube (Figure 3). The structure confirmed the heterodinuclear bismuth(III) lead(II) complex **1_{Bi}.PbOAc**, with bismuth and lead cations located on opposite sides (Bi-Pb 3.802 Å), and in which only the bismuth cation is bound to the porphyrin N-core. The coordination modes of both bismuth and lead acetate are almost the same than those observed in **1_{Bi}** and **2_{Pb}.PbOAc** and are found compatible if not complemental. The bismuth cation is seven-coordinate, 1.559 Å out of the 24MP in an antiprismatic polyhedron. It is bound to the four nitrogen atoms of the macrocycle and to the hanging carboxylate group of the strap in a bishapto fashion. The coordination sphere is completed with two molecules of DMSO maintained by hydrogen bonds with the amide groups of the straps. This distance to the 24MP of 1.559 Å is significantly larger than that in **1_{Bi}** (1.309 Å), presumably to accomodate the lead coordination on the other side. The latter adopts an inward orientation, with a strongly hemidirected coordination sphere due to the stereochemically active lone pair of lead as in **2_{Pb}.PbOAc**. The lead coordination sphere is composed of an intramolecular carboxylate counterion from the strap, an exogenous acetate counteranion and a DMSO ligand. The acetate and DMSO molecules are stabilized by H-bonds with the amide groups of the strap. Lead is HAT-bound 2.231 Å over the 24MP, and does not interact with the N-core with its lone pair pointing towards the center of the N-core of the macrocycle.

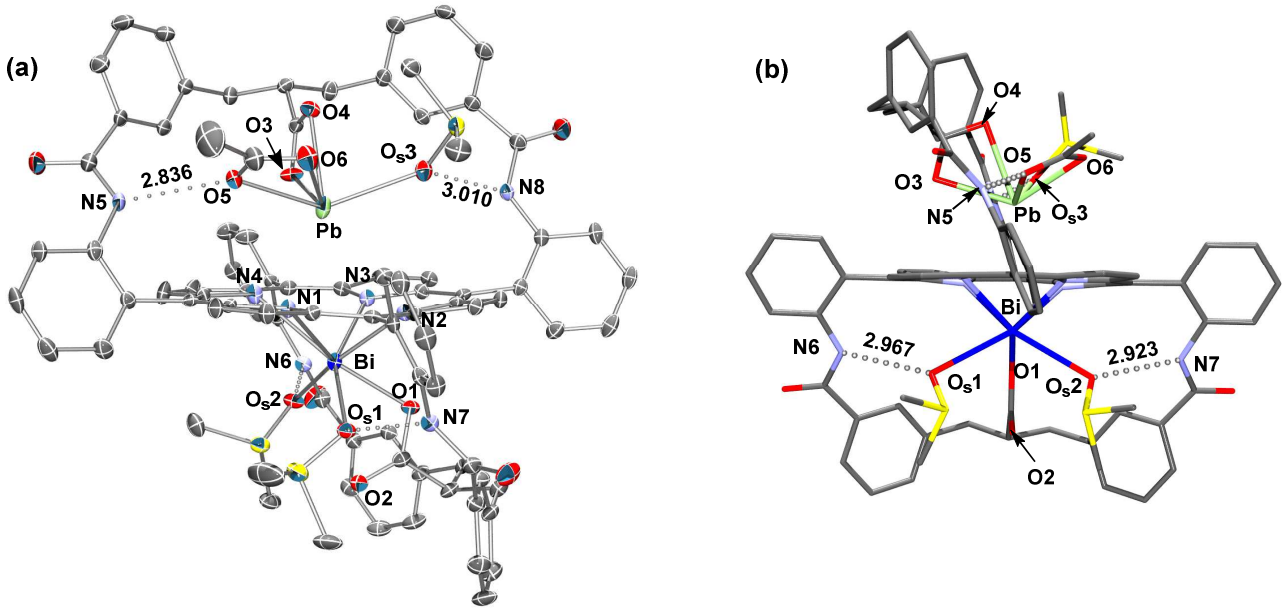
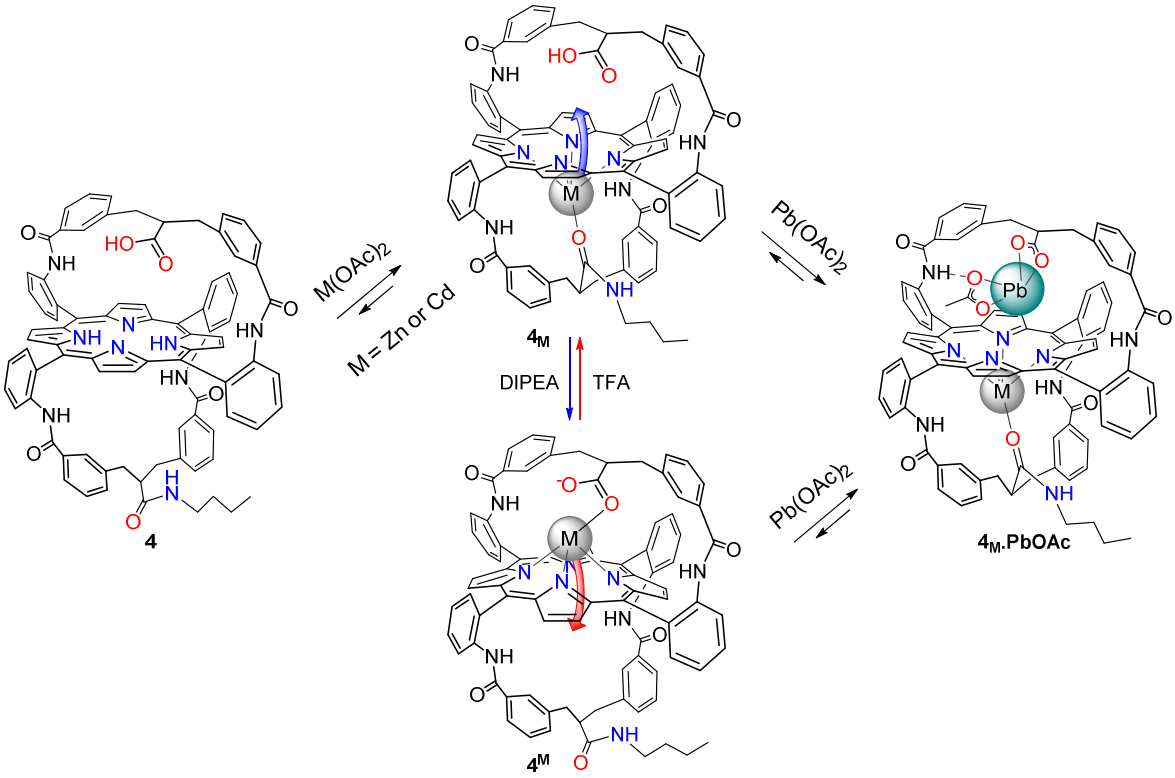


Fig. 3. X-ray structure of heterobimetallic lead complex **1_{Bi}.PbOAc**. (a) perspective ORTEP view, (b) Side view indicating the bending of the strap to accomodate the HAT Pb. (Distances [Å]: Bi-24MP 1.559, Pb-24MP 2.231, Bi-Pb 3.802, N1-Bi 2.638, N2-Bi 2.342, N3-Bi 2.393, N4-Bi 2.678, O1-Bi 2.294)

As detailed in the precedent examples of complexes incorporating a HAT coordinated PbOAc moiety, this coordination mode requires at least an overhanging carboxylic acid on one side, tethered over the concave side of a dome-distorted porphyrin. So far this distortion was obtained by the OOP coordination of another lead or bismuth cation with a significant out-of-plane displacement up to 1.559 Å.



Scheme 4. Successive metalations by first zinc or cadmium acetate and then lead acetate of unsymmetrical bis strap porphyrin **4**

However, transition metals that exhibit square planar pyramidal coordination are expected to bind the N4-core of the porphyrin out of the plane as well but with a smaller displacement due to their smaller ionic radius. Investigations probing such a possibility have been carried out with bis strap porphyrin **4** (scheme 4). In the latter one of the two carboxylic acid group has been transformed in a butylamide group. Thus, it can be anticipated that in **4**, only one side is suitable for a HAT-bound lead cation.

Initially, porphyrin **4** was designed to demonstrate a possible stereoselectivity in the incorporation of transition metals such as zinc or cadmium [24]. For instance, addition of 1 equiv. of $Zn(OAc)_2$ or $Cd(OAc)_2$ led instantaneously to the quantitative formation of the corresponding mononuclear complexes (scheme 4, first step). Interestingly, it was found that the ^{1}H NMR spectra of the metallated species were affected by the presence of a base (DIPEA) particularly the signals belonging to the amide alkyl chain as the NMR shifts experienced by these amide protons are useful to probe the side of the macrocycle on which the metal ion is located. Without entering into details, without any base, zinc or cadmium is incorporated into **4** on the side of the amide chain with the carbonyl of the amide group bound to the cation as a fifth ligand. This was confirmed by the X-ray structure of $\mathbf{4_{Zn}}$. In this notation, arbitrarily, the amide strap is drawn as the bottom one and the carboxylic acid is represented as the top strap. Thus the metal written in subscripted letters indicates that it is bound to the overhanging amide group whereas, written in superscripted letters, shows its binding to the carboxylic acid group.

Additionally, when DIPEA is added to the solution of $\mathbf{4_{Zn}}$ (or $\mathbf{4_{Cd}}$), the intramolecular carboxylic acid is deprotonated in a carboxylate group, a better electron-donating group than the amide group, inducing the migration of the N4-bound metal from the other side (that of the amide group) to its own side (scheme 4, vertical equilibrium). This change of stereoselectivity from $\mathbf{4_{Zn}}$ to $\mathbf{4^{Zn}}$ is fully reversible and controlled by the acid-base conditions. The fact that $\mathbf{4_{Zn}}$ and $\mathbf{4^{Zn}}$ exist in a fast exchange regime on the NMR time scale while the metallated species and the free base are observed in a slow exchange regime rules out a switching process going through demetalation (and hence via the free base

porphyrin). Thus, this inversion of stereoselectivity is achieved by a through-the-ring motion of cations such as zinc or cadmium.

The next step (scheme 4, second step) consisted of addition of 1 equiv. of $Pb(OAc)_2$ to the related complexes $\mathbf{4^{Zn}}$ (or $\mathbf{4^{Cd}}$) in the presence of base and led to the quantitative formation of new species. On the proton NMR spectrum, the most noticeable change is represented by a highfield shift of the protons of the amide alkyl chain. This indicates an alkyl chain closer to the porphyrin macrocycle, in agreement with the migration of the Zn(II) and Cd(II) ions from *up* to *down* positions induced by the binding of PbOAc to the hanging carboxylate (HAT coordination). Concomitantly, a significant highfield shift of the average signal of AcO^- is also observed. Obviously, the same metalation with $Pb(OAc)_2$ can be also achieved starting from $\mathbf{4_{Zn}}$ (or $\mathbf{4_{Cd}}$), without any base and leads to the same complexes, without intramolecular migration of the OOP-bound metal.

The formation of these heterobimetallic complexes with zinc(II) or cadmium(II) OOP-bound to the N4-core of the porphyrin and lead(II) HAT-bound (overhung) to the strap has been confirmed by the resolution of the X-ray structures of both $\mathbf{4_{Zn}}$**.PbOAc** and $\mathbf{4_{Cd}}$**.PbOAc** (Figure 4). Both Zn and Cd atoms are located out of the porphyrin mean plane towards the amide strap at respectively 0.498 and 0.840 Å, with average N-Zn and N-Cd distances of 2.075 and 2.213 Å. The O atom of the amide group represents the fifth ligand in apical position, hence the inwards position of the alkyl chain. The coordination sphere of Zn is not much affected by the presence of a HAT Pb(II) as only a slight increase of the out-of-plane displacement is noticed (Δ24MP 0.428 Å for $\mathbf{4_{Zn}}$), which might arise from a repulsive electrostatic interaction between the two metal ions. In the case of Cd, the rather short O1-Cd distance of 2.217 Å indicates a strong interaction, responsible for the important out-of-plane displacement of the Cd atom. On the other side, the Pb atoms are overhung respectively 2.774 and 2.648 Å above the porphyrin mean plane for the Zn and Cd complexes, without interaction with the N-core (av. N-Pb 3.698 and 3.613 Å, respectively). The rather large Pb-Zn (/Pb-Cd) distance of 3.514 (/3.660) Å indicates no metalophilic interaction. As observed with all other structurally characterized HAT Pb(II) ions, the hemidirected coordination sphere of lead in $\mathbf{4_{Zn}}$**.PbOAc** and $\mathbf{4_{Cd}}$**.PbOAc** locates the metal ion at the apex of a distorted pyramid with the $6s^2$ lone pair directed towards the lightly dome-distorted porphyrin. In both cases, the coordination sphere incorporates five oxygen atoms: four from the carboxylate of the strap and from the acetate counteranion (both bound in a bis-hapto geometry), and one from a molecule of methanol. The acetate is involved in H-bonding interaction with the amide group of the strap (O4-N5 2.883 and 2.855 Å). This second sphere of coordination is crucial for the successful binding of a HAT Pb(II). As compared to other HAT Pb(II) formed with a larger OOP-bound metal ion as Pb(II), the HAT-bound Pb atom in $\mathbf{4_{Zn}}$**.PbOAc**(/$\mathbf{4_{Cd}}$**.PbOAc**) is located respectively 0.45(/0.32) Å higher relative to the porphyrin mean plane. This can be rationalized by a smaller out-of-plane displacement of Zn(II) and Cd(II)) (Δ24MP 0.50/0.84 Å *vs.* 1.383 Å for Pb(II)).

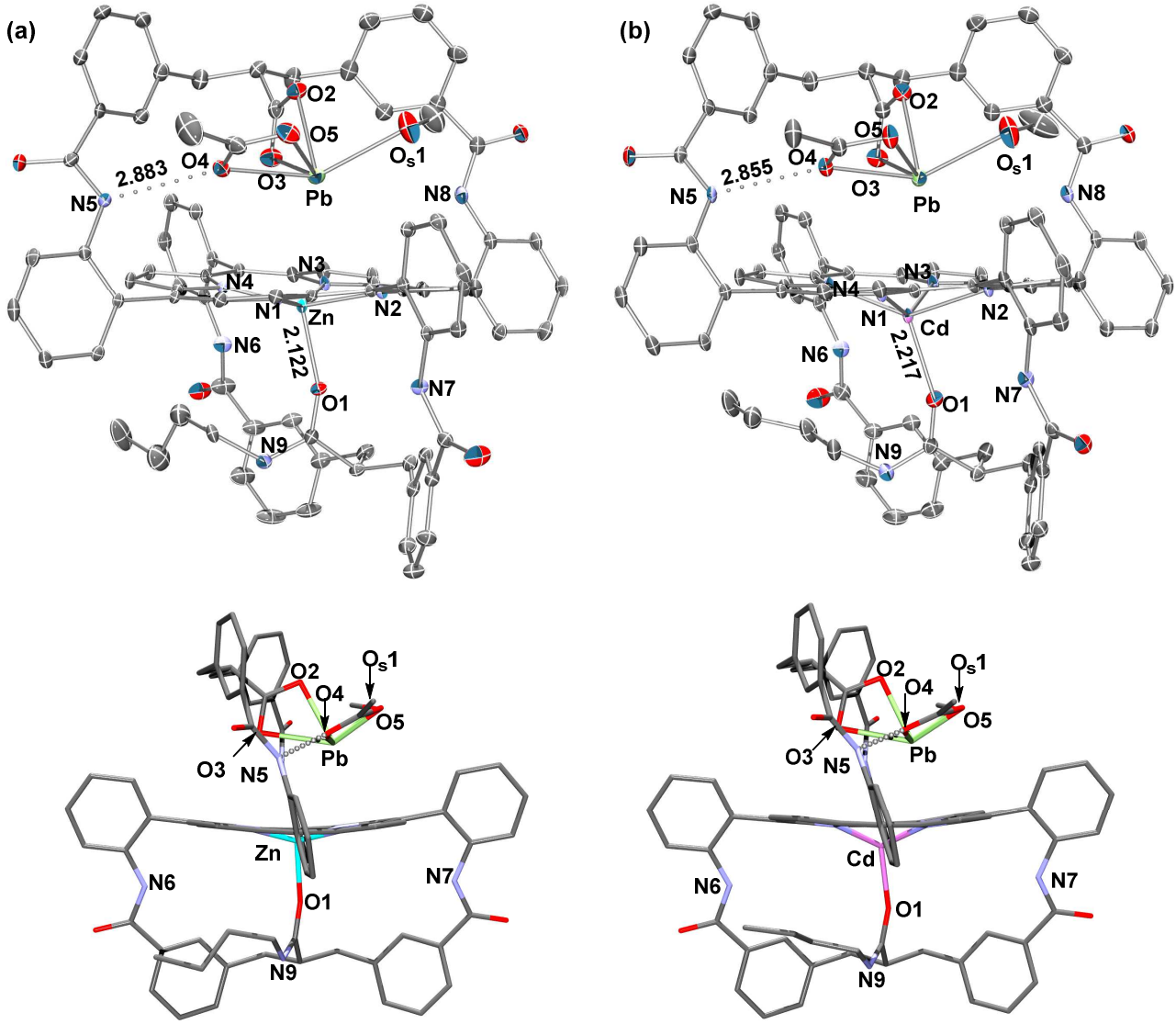


Fig. 4. X-ray structures of heterobimetallic lead complexes (a) $\mathbf{4_{Zn}}$**.PbOAc** and (b) $\mathbf{4_{Cd}}$**.PbOAc** (top line: perspective ORTEP view, bottom line: side view indicating the bending of the strap to accomodate the HAT Pb. (Distances [Å]: $\mathbf{4_{Zn}}$**.PbOAc**: Zn-24MP 0.498, N1-Zn 2.090, N2-Zn 2.079, N3-Zn 2.055, N4-Zn 2.078, O1-Zn 2.122, Zn-Pb 3.514, Pb-24MP 2.774, Pb-O2 2.316, Pb-O3 2.495, Pb-O4 2.442, Pb-O5 2.477, Pb-Os1 2.540; $\mathbf{4_{Cd}}$**.PbOAc**: Cd-24MP 0.840, N1-Cd 2.217, N2-Cd 2.223, N3-Cd 2.202, N4-Cd 2.211, O1-Cd 2.217, Cd-Pb 3.660, Pb-24MP 2.648, Pb-O2 2.337, Pb-O3 2.490, Pb-O4 2.432, Pb-O5 2.517, Pb-Os1 2.525)

B. BISMUTH DINUCLEAR PORPHYRIN COMPLEXES

1. Homobimetallic Complexes

Having isolated and fully characterized $\mathbf{1_{Bi}}$**.PbOAc**, it was very tempting to treat $\mathbf{1_{Bi}}$ with an excess of $Bi(OAc)_3$ to probe if the HAT coordination mode was only obtained with a lead(II) cation or if it could be extended to another metal. Indeed, Bi(III) being isoelectronic of Pb(II) and exhibiting a stereochemically active lone pair as well, was the perfect candidate [20].

When using $Bi(OAc)_3$, well resolved proton NMR spectra were observed (Figure 5) and a mixture of two complexes was obtained with the ratio of these species depending on the presence of a base. In the presence of DIPEA, addition of an excess of bismuth acetate to $\mathbf{1_{Bi}}$ led to a 95:5 ratio of these new complexes (Figure 5b, black and white triangles). The major species (black triangles) displays a dissymmetric NMR pattern, with highfield shifted singlets at $\delta = 0.39$ and

0.16 ppm, accounting for 3 protons each, attributed to two acetate anions located in the anisotropic current of the macrocycle, and hence HAT bound. Besides, NOE cross peaks were observed between these CH_3 signals at 0.39 and 0.16 ppm and the β-pyrrolic protons at 8.95 and 9.02 ppm, respectively. These data are in agreement with the binding of a HAT Bi(III) cation to $\mathbf{1_{Bi}}$ and the formation of the bimetallic complex $\mathbf{1_{Bi}.Bi(OAc)_2}$ (Scheme 5). Logically, two of the four NHCO protons resonate at 10.32 and 10.12 ppm as sharp singlets and are unshielded of ~ 1.5 ppm upon complexation of the HAT Bi(III) cation, for which both acetate counteranions are H-bound to the amide groups of the strap.

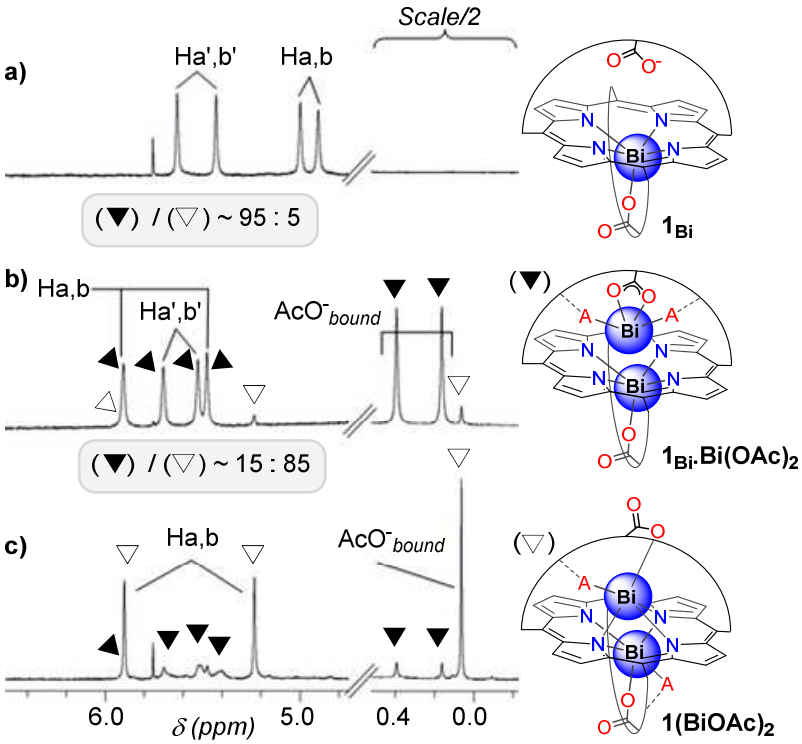
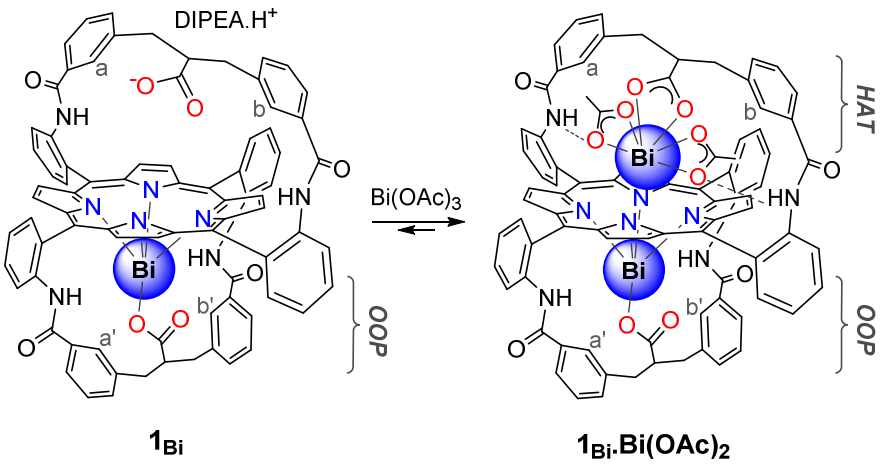


Fig. 5. ^{1}H NMR spectra (500 MHz, 298 K, DMSO-d_6) of (a) $\mathbf{1_{Bi}}$ (b) complex $\mathbf{1_{Bi}.Bi(OAc)_2}$ obtained by addition of excess of $Bi(OAc)_3$ to $\mathbf{1_{Bi}}$ in the presence of DIPEA (15 equiv.) (c) $\mathbf{1(BiOAc)_2}$ obtained by addition of excess of $Bi(OAc)_3$ to $\mathbf{1_{Bi}}$ without any base. "A" stands for "acetate"

Interestingly, if the same titration is performed without DIPEA, the "previous" minor compound becomes the major one (85 %) and the "previous" major one, namely $\mathbf{1_{Bi}.Bi(OAc)_2}$, becomes the minor one (15 %). This "new" major species exhibits a C_2-symmetric NMR signature as evidenced by two singlets at 5.90 and 5.23 ppm attributed to Ha and Hb aromatic protons of the strap (Figure 5c, white triangles). The only possibility to obtain a complex with both sides identical is to incorporate a second bismuth cation and that both cations adopt the same coordination sphere. Further analysis of the proton NMR spectrum indicates a highfield shifted singlet close to 0 ppm integrating for 6 protons, attributed to two magnetically identical acetate anions bound in the HAT mode. The downfield shift of *c.a.* 1 ppm for 2 amide NH protons, due to H-bonding interactions of the HAT acetate counteranions with one of the amide groups of the strap, confirms the proposed structure. Therefore, in this C_2-symmetric complex named $\mathbf{1(BiOAc)_2}$ (see chemical structure in Figure 5c), the NMR data indicate the binding of a BiOAc moiety on both sides of the porphyrin.

As in complex $\mathbf{1_{Pb}.PbOAc}$, it was found that each bismuth(III) cation in $\mathbf{1_{Bi}.Bi(OAc)_2}$ exchanges its coordination mode, that is adopts alternatively the HAT and OOP coordination modes as proven by exchange correlations between the signals of the "C_2 symmetrically related" protons of the two straps. This exchange is achieved via an intramolecular

mechanism involving equilibria with **1(BiOAc)$_2$** as an intermediate. Indeed, this exchange through intermolecular processes, that is through equilibria with the monometallic complex **1$_{Bi}$** and the free base **1**, would require a high energetic cost for the decomplexation of both cations. This hypothesis is not reasonable as first, **1$_{Bi}$.Bi(OAc)$_2$** is formed starting from the isolated complex **1$_{Bi}$** and second, no exchange correlation between protons of the two straps was found in the ROESY of the mononuclear complex **1$_{Bi}$** formed *in situ* by addition of 1 equiv. of Bi(OAc)$_3$ to **1**.



Scheme 5. Metalation of bis strap porphyrin **1$_{Bi}$** by bismuth acetate

An elemental analysis of an analytical sample of this complex as well as the X-ray structure obtained from crystals of **1$_{Bi}$.Bi(OAc)$_2$** grown from a chloroform/cyclohexane mixture confirmed the homodinuclear nature of this species. In the latter coexist two bismuth atoms with only one of them directly bound to the N-core of the porphyrin (Figure 6). The latter, bismuth cation Bi1, is similar to its counterpart observed in **1$_{Bi}$**. Bi1 is seven-coordinate 1.310 Å out of the 24-atom porphyrin mean plane (24MP) with an average N-Bi bond length of 2.375 Å. It is worth to note that its distance to the 24MP is the same than that in **1$_{Bi}$** (1.309 Å) but different than that in **1$_{Bi}$.PbOAc** (1.559 Å). Whether it is due to a difference in the size of these two cations or the difference in the activity of their lone pair is still to be investigated [25,26]. Bi1 is also bound to a hanging carboxylate group of the strap in a mono-hapto fashion (O1-Bi, 2.491 Å), and to two water molecules (O_w1 and O_w2). One of them (O_w1) is stabilized by a hydrogen bond with the O2 atom of the overhanging carboxylate group (O_w1-O2, 2.808 Å). A second bismuth cation Bi2 is coordinated on the opposite side of the porphyrin but without any direct interaction with the N-core (Bi2-24MP, 2.576 Å; average N-Bi distance, 3.409 Å). Indeed, it is bound in a bis-hapto mode to the overhanging carboxylate group (O3/O4) and to two acetate counteranions (O5/O6 and O7/O8). The latter are maintained by hydrogen bonds with the amide groups of the strap (N5-O5, 2.912 Å and N8-O7, 2.837 Å). The plane of each acetate group is almost perpendicular to that of the intramolecular carboxylate group, thereby defining a strongly hemidirected coordination sphere of Bi2 with an *inward* orientation. In light of this dinuclear bismuth structure and together with the previously reported structure of the dinuclear lead complex **2$_{Pb}$.PbOAc**, the HAT coordination mode appears quite versatile with a coordination site composed of a carboxylate group dangling over the concave face a dome-shaped metalloporphyrin, with a crucial role of the second coordination sphere brought by the strap itself.

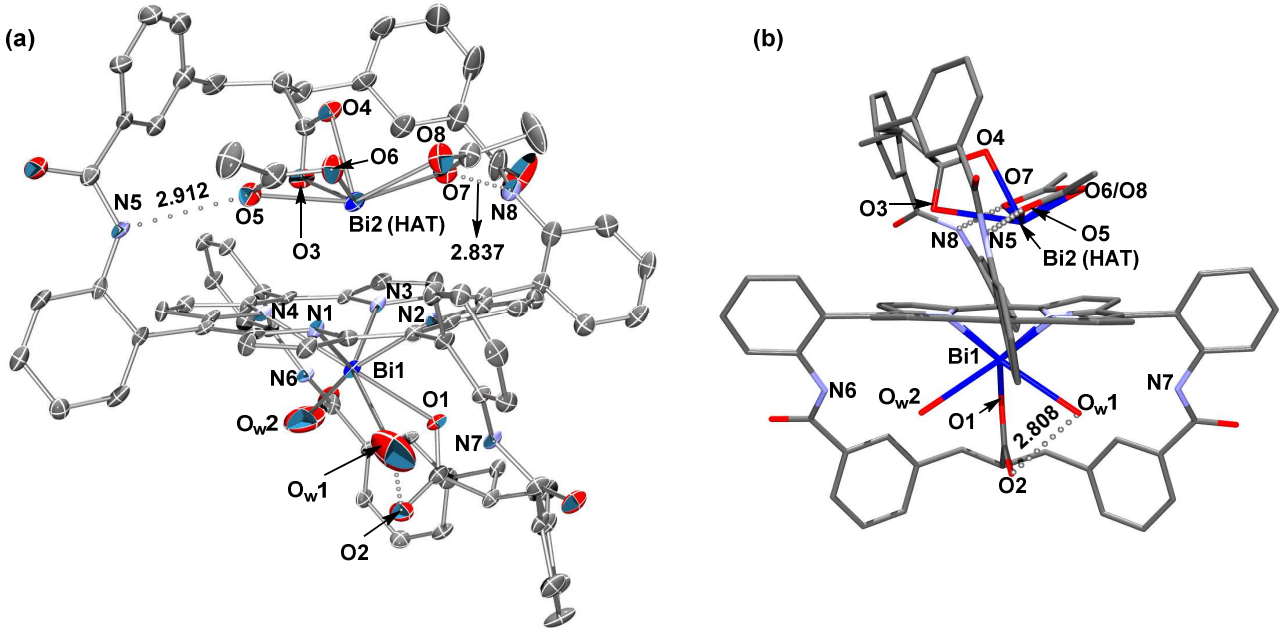


Fig. 6. X-ray structure of homobimetallic bismuth complex $\mathbf{1_{Bi}.Bi(OAc)_2}$. (a) Perspective ORTEP view, (b) side view indicating the bending of the strap to accomodate the HAT Bi. (Distances [Å]: Bi1-24MP 1.310, Bi2-24MP 2.576, Bi1-Bi2 3.932, N1-Bi1 2.429, N2-Bi1 2.306, N3-Bi1 2.331, N4-Bi1 2.442, O1-Bi1 2.491, O3-Bi2 2.493, O4-Bi2 2.212, O5-Bi2 2.487, O6-Bi2 2.292, O7-Bi2 2.551, O8-Bi2 2.260)

2. Heterobimetallic complexes

The only heterobimetallic bismuth porphyrin complex characterized in the solid state by an X-ray structure was obtained with lead as $\mathbf{1_{Bi}.PbOAc}$ and has been discussed in section A2.

C. MERCURY DINUCLEAR PORPHYRIN COMPLEXES

1. Homobimetallic Complexes

When octaalkyl porphyrins such as aetioporphyrin or coproporphyrin are metalated by mercury acetate in pyridine, a regular one-to-one complex is obtained. At the opposite, if the same reaction is performed in methylene chloride or THF, the proton NMR spectrum of the resulting complex exhibits an upfielded singlet around 0 ppm accounting for 3 protons per porphyrin. This signal is consistent with an acetate group residing in the anisotropic ring-current of the porphyrin. The elemental analysis suggested a composition of two porphyrins, three mercury atoms, and two acetate functions, consistent with a double-sandwich trimetallic structure AcO-Hg-Por-Hg-Por-Hg-OAc [27]. A third type of complex is obtained under the same experimental conditions with tetraphenylporphyrin (TPP). Indeed, because of steric reasons, the "double-sandwich" structure was not stable enough and, on the evidence of elemental analysis, a true symmetric homobimetallic mercury complex was proposed [28,29]. In this complex, formally, a HgOAc is coordinated on each side of the macrocycle via one σ-bond and one π-bond (Figure 7) [30], leading among others to a sharp singlet of 6 protons at 0.56 ppm on the proton NMR spectrum. In the absence of X-ray structure, this type of bimetallic complex has been very useful to investigate metal transfer processes that occur during demetalation.

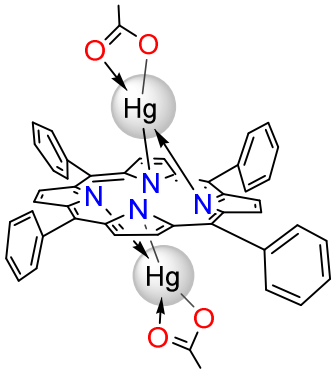


Fig. 7. Chemical structure of the first bimetallic mercury complex **TPP(HgOAc)$_2$** proposed by Smith

Since this pionering work of Smith, no other example of dinuclear complexes have been reported with naked or non functionalized porphyrins. However, more recently, the coordination chemistry of bis strap porphyrin **1** towards mercury was investigated [31]. First, when **1** was metalated with a 3 equivalent excess of mercury acetate, the resulting mercury complex was isolated by precipitation with pentane and its elemental analysis revealed a 1:2 **1**/Hg stoichiometry, consistent with a dinuclear complex, named **1Hg$_2$**. An X-ray structure of the latter complex was obtained and is represented in Figure 8.

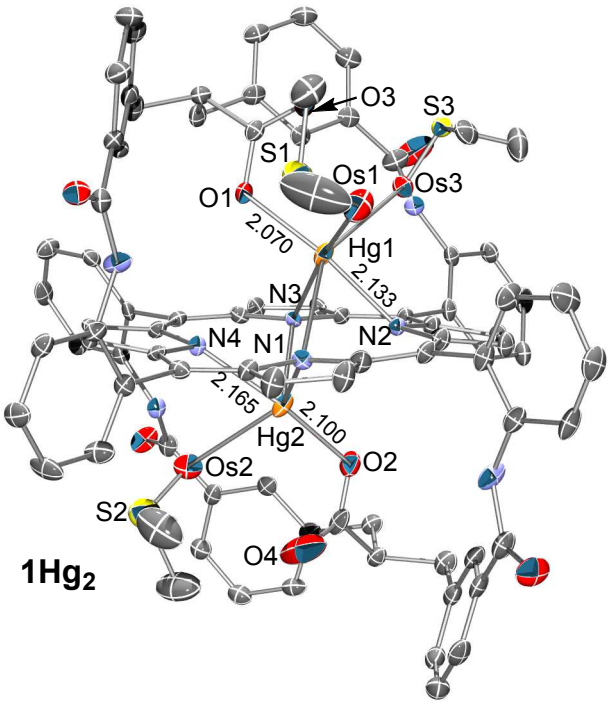


Fig. 8. X-ray structure of homobimetallic mercury complex **1Hg$_2$**. (distances [Å] and angles [°]: Hg1-Hg2 3.258; Hg1(/Hg2) to 24-atom mean plane 1.733(/1.408); N2-Hg1-O1 166.2; N4-Hg2-O2 161.3; (PyrN4-5MP, 24MP 7.8) ; (PyrN2-5MP, 24MP 8.3))

The structure reveals a dinuclear complex with a mercury ion coordinated out of the plane on each side of the macrocycle. **1Hg$_2$** is not symmetric at all as the two metal ions are located in two different environments. The two sides of the porphyrin mainly differ not only by the conformation of the two straps, the strap with Hg1 being more twisted than the strap with Hg2, but also by the *out-of-plane* position of Hg1 and Hg2 that are located 1.733 Å and 1.408 Å from the 24-atom mean plane, respectively. At first glance, the metal ions appear to be in a trigonal antiprismatic coordination polyhedron, Hg1 being six-coordinate but Hg2 being five-coordinate. For Hg1, the polyhedron is

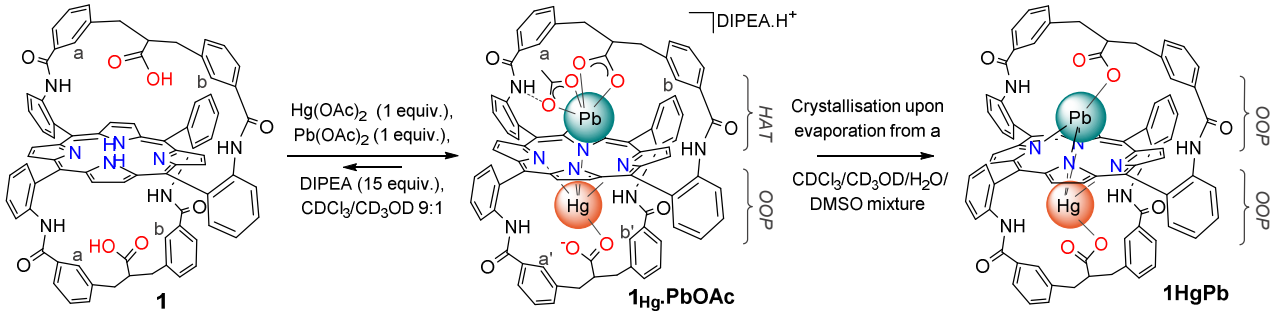
composed of three nitrogen atoms from the porphyrin (N1, N2, N3), one monohapto carboxylate group (O1) and two DMSO molecules from the solvent of crystallization (Os1 and Os3). In the case of Hg2, this polyhedron incorporates only one DMSO molecule but is also described by three nitrogen atoms from the macrocycle (N1, N3, N4), one monohapto carboxylate group (O2) and one DMSO molecule (Os2) (Figure 8). Each mercury atom exhibits two short bond distances, one with a nitrogen atom of the porphyrin and the other with an oxygen atom of the hanging carboxylate function (Hg1-N2 = 2.133 Å, Hg1-O1 = 2.070 Å, Hg2-N4 = 2.165 Å and Hg2-O2 = 2.100 Å). All the other contacts are much longer and should be considered mainly as electrostatic interactions with both the nitrogen atoms of the porphyrin and the oxygen atom of the DMSO molecules. Moreover, the angles O1-Hg1-N2 and O2-Hg2-N4 are close to 180° (166.2° and 161.3°, respectively). Therefore, a linear coordination (14-electron ML_2-type complex) is a better description for both mercury atoms in the complex **$1Hg_2$**. Actually, the X-ray structure of **$1Hg_2$** can be seen as a faithfull picture of the structure of **TPP(HgOAc)$_2$** proposed some fourty years before by Smith (Figure 7) [30].

In solution the coordination behavior of **1** is interesting as well. In proton NMR spectroscopy ($CDCl_3$, 298 K) both the free base and the isolated **$1Hg_2$** complex display a C_2 symmetrical pattern. The β-pyrrolic protons appear as two doublets and two singlets, and the four protons labeled H_a and H_b (scheme 1) resonate as two singlets showing that in both cases the two straps are equivalent. Insights into the formation of the bimetallic complex came from titration experiments both in the presence of base and without any base. As porphyrin **1** bears an overhanging carboxylic acid group on each side, it was reasonned that the presence of a base could influence the metalation process. Titration of **1** by $Hg(OAc)_2$ was performed in a low-coordinating medium ($CDCl_3/CD_3OD$ 9:1) in the presence of diisopropylethylamine (DIPEA). A two-step process leading finally to **$1Hg_2$** was observed, with the formation of an intermediate species of apparent C_2 symmetry consistent with the mononuclear complex **1Hg**. The C_2 symmetry of the NMR pattern of **1Hg** is rather surprising as one would have expected a differentiation of the two straps due to the out-of-plane coordination of Hg^{II} as reporetd elsewhere [32]. As a result, this observation implies a fast exchange process on the NMR time scale of the Hg^{II} ion between the two sides of the ligand. However, when the titration was performed without any base, a single step process leading to **$1Hg_2$** was observed and the intermediate mononuclear complex was not detected. This denotes a highly cooperative insertion of the two metal ions with an overall strong binding. This positive cooperativity can be rationalized by a low stability of the mononuclear complex in the absence of a base. Indeed, as in **1Hg** the mercury ion must be four-coordinate to the N_4-core of the macrocycle, the overhanging carboxylic groups of the straps can protonate the complex which hence becomes relatively unstable. Conversely, in **$1Hg_2$** both carboxylate groups being involved in the mercury coordination, the intramolecular protonation is no longer possible.

2. Heterobimetallic Complex

In the course of the previous titration experiment, in the presence of DIPEA, a mononuclear mercury(II) complex was formed. This implies that formally, if a second equivalent of another, properly chosen, metal salt is added, a heterobimetallic complex including one mercury cation could be isolated. In fact, the metalation reaction monitored by proton NMR spectroscopy was thus performed in the presence of 15 equiv. of DIPEA by addition of 1 equiv. of $Pb(OAc)_2$ to **1** followed by 1 equiv. of $Hg(OAc)_2$ [33]. It led to the selective formation of a new species with no trace at all of monometallic complexes and only a trace of **1_{Pb}.PbOAc** (see section A1). The four aromatic protons of the straps Ha, Hb, Ha' and Hb' (Scheme 6) resonate as four signals between 5.8 and 5.2 ppm. This clearly shows the formation of a dissymmetric species bearing a different metal ion on each side of the macrocycle. The observation of a broad and slightly highfield shifted signal for the acetate anions indicates that they take part in the complex, in a fast exchange

regime at room temperature. However low temperature NMR measurements (223 K) revealed a single bound acetate observed as a singlet at +0.18 ppm. This chemical shift is in perfect agreement with the presence of a hanging-atop metal ion. More particularly, it is consistent with a PbOAc moiety hung over the N-core, as deduced from comparison with the chemical shifts of the bound acetate in the known complex **1_{Pb}.PbOAc** formed in the same experimental conditions. Therefore the formation of the heterobimetallic complex **1_{Hg}.PbOAc** was proposed (Scheme 6, first step). The incorporation of 'HgPbOAc' in **1** was confirmed by HRMS analysis.



Scheme 6. Synthesis of mercury(II) / lead(II) heterobimetallic complexes. First step: Selective formation of **1_{Hg}.PbOAc** obtained by ^{1}H NMR titration. Second step: Preparation of the neutral complex **1HgPb** by crystallisation for XRD analysis

Upon solvent evaporation, the solution coming from the previous NMR analysis to which were added water and DMSO gave rise to crystals suitable for XRD. As for **1_{Pb}.PbOAc** that crystallized as **$1Pb_2$**, **1_{Hg}.PbOAc** crystallized by releasing its acetate moiety as the crystallographic structure revealed the formation of **1HgPb**, the neutral heterobimetallic complex in which the porphyrin bridges the two metal cations (Figure 9). Each metal ion is OOP-bound to the N-core and to the carboxylate group of a strap. The lead cation is six-coordinate and located 1.856 Å away from the 24-atom mean plane. It is bound to the three nitrogen atoms N1, N2 and N3 of the macrocycle with quite similar bond lengths: N1-Pb = 2.833 Å, N2-Pb = 2.610 Å and N3-Pb = 2.701 Å. It is also bound to the intramolecular carboxylate group of the strap and to two DMSO molecules stabilized by H-bonds with the amide groups of the straps. The coordination sphere of the lead cation in this heterobimetallic complex can be compared to that of the homobimetallic C_2-symmetric complex **$1Pb_2$** (Figure 1). The major difference is represented by the longer length of the N2-Pb-bond in **1HgPb** (2.610 Å) *vs.* 2.480 Å in **$1Pb_2$**, suggesting that the lead cation is more loosely bound in the heterobimetallic complex than in the homobimetallic one. Concerning the other side of the complex, the Hg atom undergoes a similar deviation from the mean plane (1.55 Å). The Hg atom is 6-coordinate in **1HgPb**, with three bonds to the N-core of the macrocycle (N1-Hg = 2.440 Å, N3-Hg = 2.661 Å, N4-Hg = 2.439 Å), one bond to the intramolecular carboxylate group (O1-Hg = 2.282 Å) and two bonds with DMSO and methanol molecules (Os1-Hg = 2.697 Å, Os2-Hg = 2.894 Å). The DMSO and methanol molecules bound to Hg are also stabilized by H-bonds with the amide groups of the straps. The present structure of **1HgPb** can also compare with the structure of the corresponding other homobimetallic complex **$1Hg_2$** (Figures 8 and 9c). In **$1Hg_2$**, a dissymmetric complex in the solid state, the mercury cation labeled Hg2 is the most similar to Hg in **1HgPb** (both are 6 coordinate). However, the OOP displacement of the mercury cation in **1HgPb** (1.549 Å) is roughly midway as compared to those in **$1Hg_2$** (1.41 and 1.73 Å). A main difference consists in the two σ-bonds of the mercury cations that are much longer in **1HgPb** (2.440/2.282 Å) than in **$1Hg_2$** (2.165/2.100), with a different spatial arrangement. They are in a trans geometry in **$1Hg_2$** (N2-Hg1-O1 = 166 °; N4-Hg2-O3 = 161 °), whereas a cis arrangement is observed in **1HgPb** (N4-Hg-O1 = 85 °), a more unusual coordination geometry for mercury.

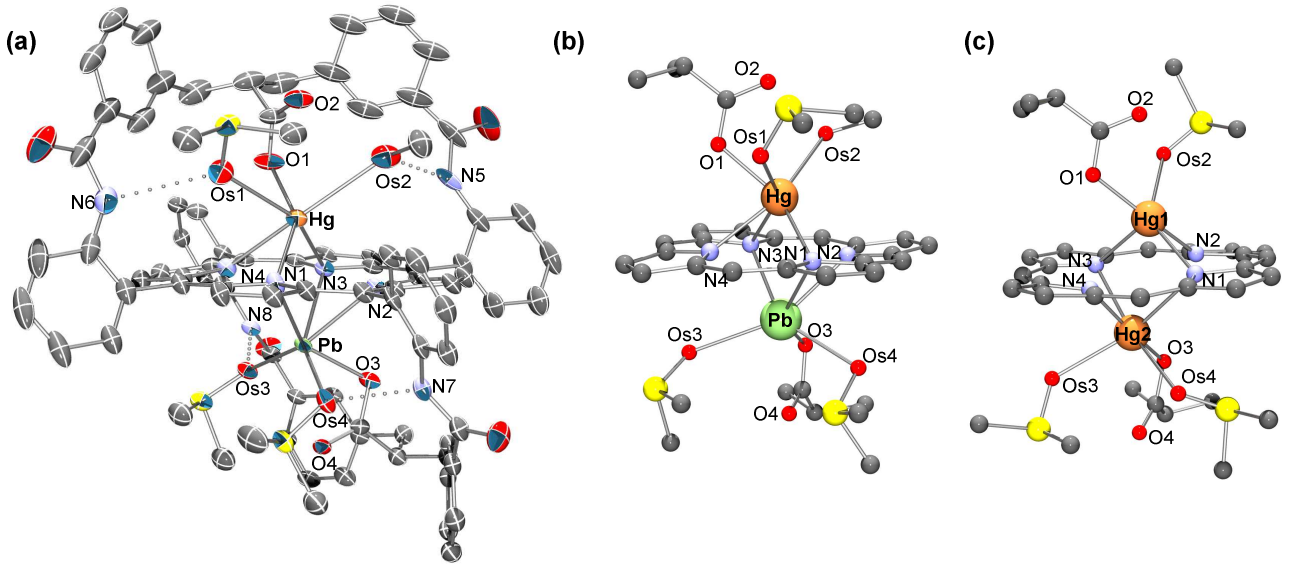


Fig. 9. X-ray structure of heterobimetallic mercury lead complex **1HgPb**. (a) Perspective ORTEP view. (b) zoomed view of the coordination sphere of **1HgPb** for comparison with (c) the coordination sphere of **1Hg$_2$**. (distances [Å] and angles [°]: Hg-Pb 3.411; Hg(/Pb) to 24-atom mean plane 1.856 (/1.549); N4-Hg-O1 82.8; N2-Pb-O3 80.7; (PyrN2-5MP, 24MP) 7.8 ; (PyrN4-5MP, 24MP) 8.3))

D. THALLIUM DINUCLEAR PORPHYRIN COMPLEXES

1. Homobimetallic Complexes

On the one hand, the first X-ray structures of mononuclear thallium(III) porphyrins were reported in 1977 by Smith [34] as well as Henrick [35] for OEP and TPP, respectively. On the other hand, since the initial work of Rothemund relative to the incorporation of thallium(I) into a porphyrin, thallium(I) porphyrins were forsaken as considered unstable [36]. However, in 1980, Smith, again, reported the synthesis of thallium(I) complexes of both OEP and TPP [37]. The complexes were obtained by treatment of the free base by thallium(I) ethoxide in THF as stable and pure precipitated compounds, based on elemental analysis which indicated bis-thallium complexes ! Upon further analysis of their proton NMR spectra which showed no evidence of non-equivalence of the two sides of the porphyrin, the authors proposed a symmetrical structure bearing a thallium(I) cation singly bound to the N-core on each side of the porphyrin (Figure 10, inset). They came back to this research topic in 2001, applied the same method of insertion, and finally fathomed the mystery with the X-ray structure of the homobimetallic thallium(I) complex of OEP, namely **[(THF)Tl(I)]$_2$(OEP)** (Figure 10) [16]. Formally, the complex is a μ-[porphyrinato]bis[tetrahydrofuranthallium(I)] as the porphyrin acts as a bridging ligand between the two thallium(I) cations. There are two Tl(I) cations, one on each side of the porphyrin with three bonds to nitrogen atoms from the pyrroles and a fourth bond to the oxygen atom of an apical THF ligand. The two N2 and N2' to thallium bonds are much longer than the N1-Tl one. Partly based on the Tl-Tl distance of 3.29Å, the authors proposed no interaction between the two cations. The porphyrin ring is distorted in a wave form with the two opposite pyrrole rings σ-bound to the thalliun ions tilted by 12° relatively to the 24-atom mean plane of the porphyrin. The coordination geometry of each thallium ion in this complex appears as a distorted trigonal bipyramid. As the apical positions are occupied by N1 and O, and two of the equatorial sites by N2 and N2', it was concluded that the lone pair of Tl(I), obviously stereochemically active in this case, occupies the third equatorial site. To the best of our knowledge, this X-ray structure remains the unique instance of a homobimetallic Tl(I) porphyrin complex.

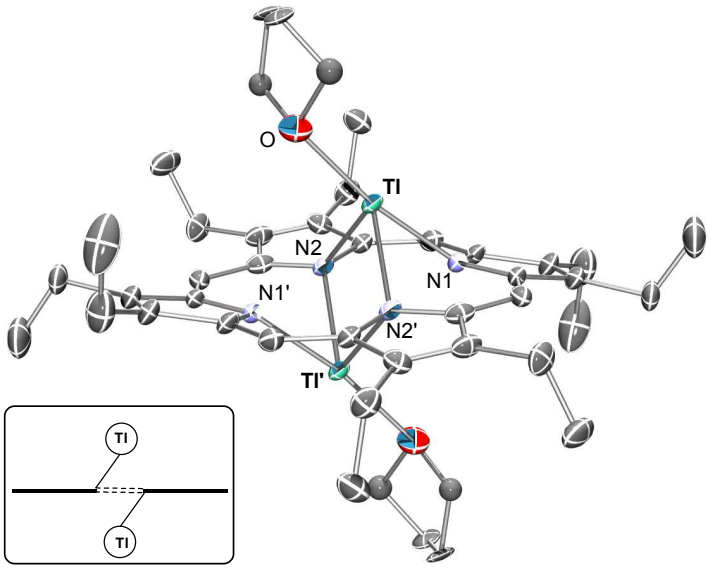
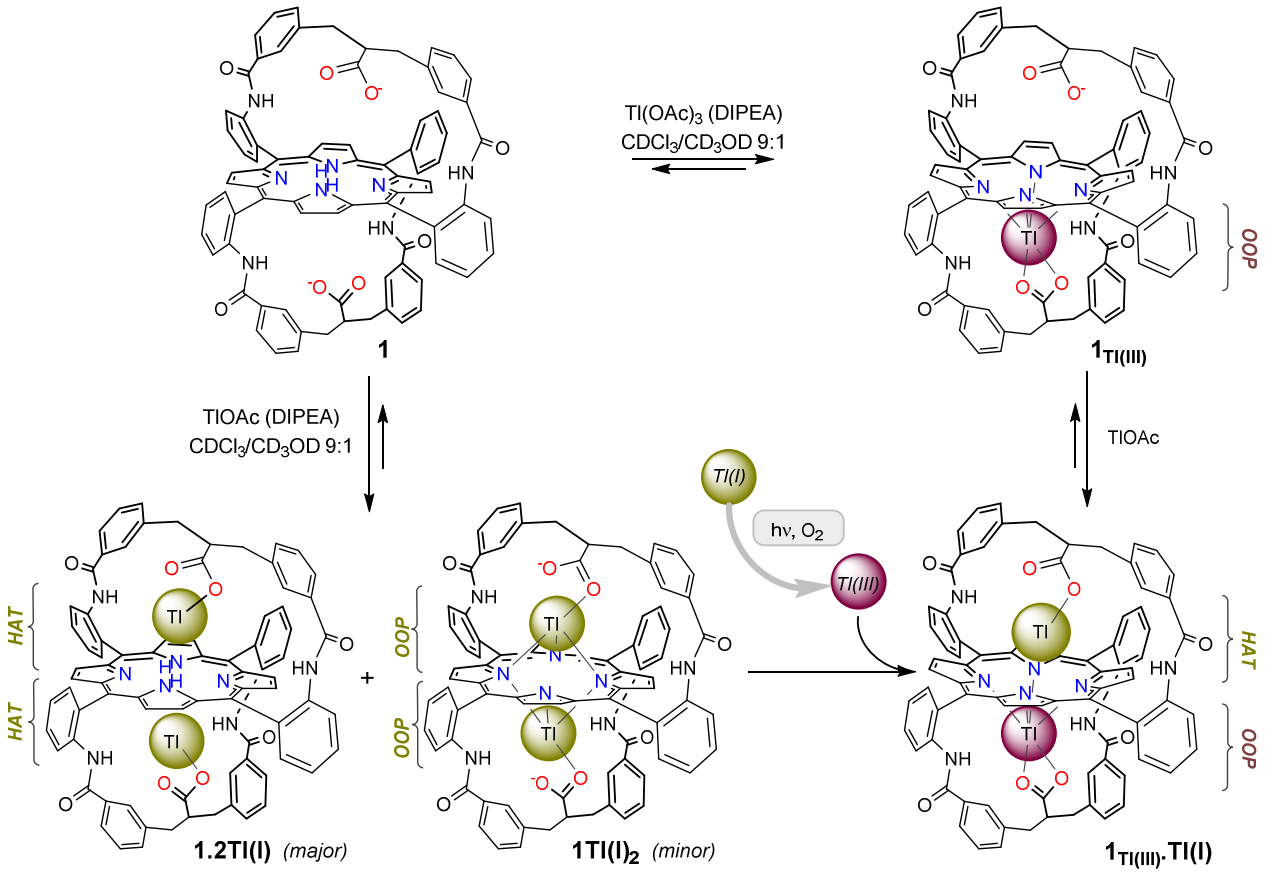


Fig. 10. Very first structure and still unique X-ray structure of homobimetallic thallium(I) complex **[(THF)Tl(I)]$_2$(OEP)**. (distances [Å] and angles [°]: N1-Tl 2.129; N2-Tl 2.597; O-Tl 2.136; Tl-Tl 3.297; Tl to 24-atom mean plane 1.597; N1-Tl-O 170.93; (PyrN2-5MP, 24MP) 7.8 ; (PyrN1-5MP, 24MP) 12.42)). Inset: reproduction of Smith's 1980 initial representation of bis-thallium(I) porphyrin complex

Thallium(III) porphyrin coordination being relatively comparable to that of bismuth(III), the formation of possible homobimetallic thallium(III) complexes was recently investigated with bis strap porphyrin **1**. In a $CDCl_3/CD_3OD$ 9:1 solution, the monometallic Tl(III) complex $\mathbf{1}_{\mathbf{Tl(III)}}$ was readily obtained by addition of a slight excess of $Tl(OAc)_3$ to **1** but conversely to what was observed with bismuth acetate, no other species were detected with a higher amount of the metal salt (scheme 7, top line). The dissymmetric ^{1}H NMR distribution indicates that Tl(III) is located on one side of the macrocycle, and this was confirmed by the X-ray structure of $\mathbf{1}_{\mathbf{Tl(III)}}$ [23]. It was demonstrated that in solution an intraligand exchange of Tl(III) between the two sides of the macrocycle occurs by funneling through the N-core as a ROESY 2D NMR experiment shows exchange correlations between protons of opposite straps. Thus, the complex exists as two degenerate states ($\mathbf{1}_{\mathbf{Tl(III)}}$ / $\mathbf{1}^{\mathbf{Tl(III)}}$) in fast exchange regime while the free base **1** and $\mathbf{1}_{\mathbf{Tl(III)}}$ are in slow exchange regime. In a second step, addition of TlOAc to a solution of $\mathbf{1}_{\mathbf{Tl(III)}}$ led to a clear modification of the ^{1}H NMR spectrum consistent with the complexation of Tl(I) in a fast exchange regime. In the presence of DIPEA, a broad C_2-symmetric NMR signature with characteristic $H_{\beta pyr}$-Tl(III) ^4J coupling constants of ~63 Hz was observed (scheme 7, right vertical equilibrium). An X-ray structure of this species was resolved and revealed the formation of a mixed valence Tl(III)/Tl(I) complex, namely $\mathbf{1}_{\mathbf{Tl(III)}}$**.Tl(I)**, owing to the binding of Tl(I) to the free overhanging carboxylate group of $\mathbf{1}_{\mathbf{Tl(III)}}$ (Figure 11). Tl(I) stands 2.973 Å above the 24MP with no interaction with the N-core and with a Tl(III)-Tl(I) distance of 4.072 Å. Its coordination sphere involves five oxygen atoms which are O3 and O4 of the overhanging carboxylate, $O_{(MeOH)}$ of a weakly bound methanol which is further stabilized by a hydrogen bond with an amide group of the strap (dashed line, 2.968 Å), O3 of a second complex (intermolecular coordination) leading to a dimeric assembly inside the crystal. $\mathbf{1}_{\mathbf{Tl(III)}}$**.Tl(I)** is the first example of mixed-valence thallium(III)/(I) reported so far [23].



Scheme 7. Synthesis of the first mixed valence Tl(III)/Tl(I) dinuclear porphyrin complex according to two different pathways

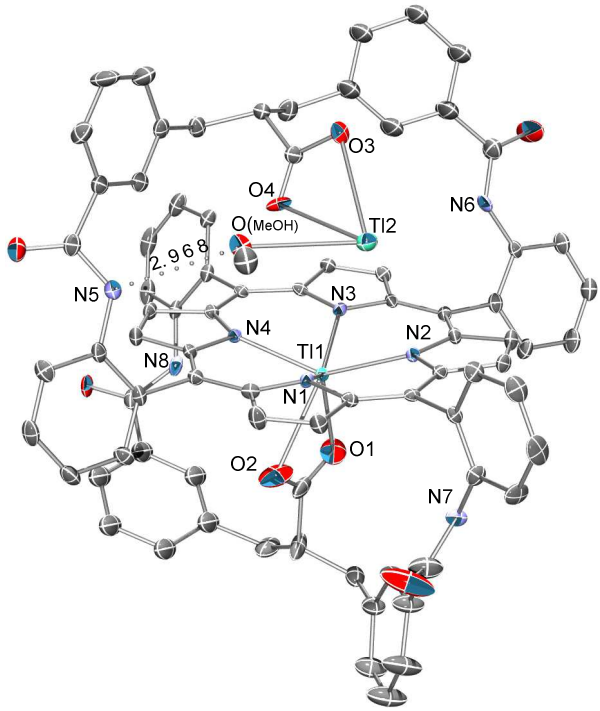


Fig. 11. X-ray structure of homobimetallic thallium(I)/thallium(III) complex $\mathbf{1_{Tl(III)}.Tl(I)}$. (distances [Å]: Tl1-N1 2.240, Tl1-N2 2.219, Tl1-N3 2.235, Tl1-N4 2.204, Tl1-O1 2.267, Tl1-O2 2.588, Tl1-24MP 0.826, Tl1-Tl2 4.072, Tl2-24MP 2.973, Tl2-O3 2.679, Tl2-O4 2.719, Tl2- $O_{(MeOH)}$ 2.897, Tl2-O3 (inter) 2.762

In solution, a 2D NMR ROESY experiment of $\mathbf{1_{Tl(III)}.Tl(I)}$ shows exchange correlations between protons of the two straps as for $\mathbf{1_{Tl(III)}}$ indicating that the metal ions exchange their position relative to the porphyrin plane. This equilibrium between the two degenerate forms of the complex corresponds to a double translocation that implies an intramolecular motion for Tl(III) through the N-core with an intermolecular pathway for Tl(I) exchanging between the two overhanging carboxylate groups.

Considering the previous work of Smith [16] about the metalation by thallium(I) salt, it was also of interest to metalate porphyrin **1** with TlOAc. Thus, this metalation was achieved in the same conditions than for thallium(III) salt, in $CDCl_3/CD_3OD$ solution and in the presence of DIPEA. A mixture of two species was obtained with 5 equiv. of TlOAc. At 298 K, the major one displays an ill defined spectrum whereas a well resolved C_2-symmetric signature is observed for the minor one (scheme 7, left vertical equilibrium). A similar titration experiment done by UV-visible spectroscopy indicates that the major species presents a Soret band slightly red shifted as compared to **1** (430 *vs.* 421 nm), whereas that of the C_2-symmetric species is observed at 488 nm. These data are in agreement with those reported by Smith [16] and consistent with a mixture of two bimetallic complexes, namely **1.2Tl(I)** and $\mathbf{1Tl(I)_2}$, for which the two Tl(I) are bound respectively in a fast exchange regime to the strap (HAT) and in a slow exchange regime to the N-core (OOP). Unfortunately, no X-ray structure of any of these two complexes have been obtained, so far. Nevertheless, an intriguing photo-redox process requiring dioxygen (ambient atmosphere) leads to the transformation of the previous mixture of thallium(I) bimetallic complexes in the mixed valence complex $\mathbf{1_{Tl(III)}.Tl(I)}$ (scheme 7, bottom line).

2. Heterobimetallic Complexes

Although mercury(II)-thallium(I) heterobimetallic complexes have been very recently investigated in solution with bis-strap porphyrin **1** and were shown to undergo spontaneous Tl(I)-to-Tl(III) oxidation [38], to date, the only known X-ray structure is that of $\mathbf{(OEP)_2Pr(III)Tl(I)}$ [39]. It describes a very peculiar complex in which praseodymium(III) is sandwiched between two OEP units while a thallium(I) cation is bound to the N core of one of the two porphyrins on the other side, with a Pr-Tl distance of 3.514 Å (Figure 12). This complex is heterobimetallic and dinuclear, but can be regarded as a mononuclear complex from the point of view of the thallium coordination as the latter is linked to a single porphyrin unit with one N2-Tl bond shorter than the three others. In that compound praseodymium(III) and thallium(I) ions are located on opposite sides of one of the two porphyrin rings.

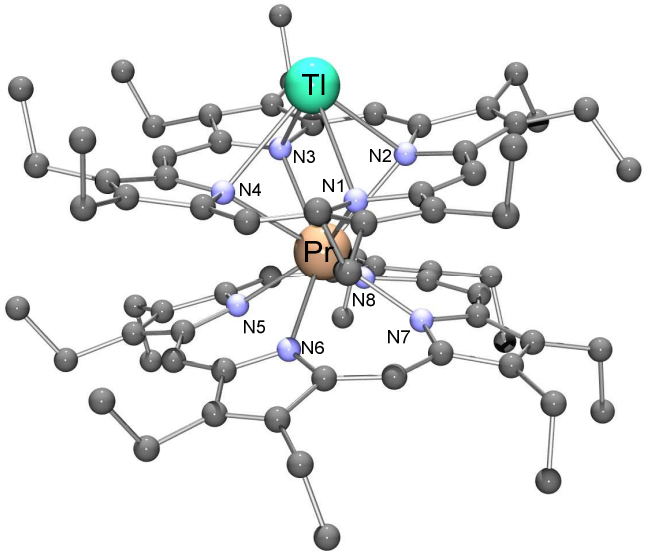


Fig. 12. X-ray structure of a heterobimetallic thallium(I)/praseodimium(III) complex (**OEP)$_2$Pr(III)Tl(I)**. (distances [Å]: Tl-N1 2.754, Tl-N2 2.638, Tl-N3 2.754, Tl-N4 2.788, Tl-Pr 3.514, Tl-24MP 1.621

CONCLUSION

For more than half a century now, porphyrin coordination chemists have investigated various ways to take profit of the particular properties of this macrocycle towards biological metals. However, the simple adjunction of supplemental coordinating groups around or, as shown herein, above the porphyrin coordination site has opened both a new static coordination chemistry and unprecedented dynamic behaviors. Although the static coordination chemistry of peculiar bimetallic complexes represents the skeleton of this minireview, it becomes obvious that both the dynamic processes by which these bimetallic complexes are formed and the resulting structures are the basis of a new area in the supramolecular coordination chemistry of porphyrins. It can be foreseen that for instance, exchange processes between different modes of coordination inside bimetallic porphyrin complexes could lead to adaptable and/or switchable new materials. This is one of the reason why a detailed analysis of their structures remains of paramount importance besides the knowledge of their dynamic behaviors.

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